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16 ABSTRACT

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JOURNAL ARTICLE

Evaluation of the Sodium Arsenite Method for Measurement of NO_2 in Ambient Air

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The sodium arsenite method for measurement of nitrogen dioxide in ambient air was evaluated. The method has a constant high collection efficiency (89%) for nitrogen dioxide, and is insensitive to normal variations in operating parameters. Nitric oxide and carbon dioxide are positive and negative interferents, respectively. The combined average effect of these interferents, over ambient levels, is a positive bias of 9.9 μg/m³. This bias, although statistically significant, is minor (10%) in relation to the ambient air standard of 100 μg NO_2/m³ and does not warrant modification of the method to remove the interferences.

Since the promulgation by the Environmental Protection Agency (EPA) of the reference method for determination of nitrogen dioxide (NO_2) in the atmosphere,[1] EPA researchers[2] and others[3-5] have determined that the method has a variable non-linear collection efficiency and a positive nitric oxide (NO) interference, rendering it unreliable. After further evaluation, the EPA Administrator, on June 14, 1973, stated that the reference method for measuring NO_2 was unreliable and would be withdrawn. EPA then selected five candidate procedures to replace the original method. Three methods involved integrated 24 hour sampling systems: an arsenite-alkaline,[6] a triethanolamine-guaiacol-sulfite,[7] and a triethanolamine[8] procedure. Two were continuous methods: a colorimetric Saltzman, and a chemiluminescent procedure.[9] Subsequently, a program of laboratory evaluation and collaborative testing of each of the five methods to determine their reliability was initiated.

The laboratory evaluation of the arsenite procedure is the subject of this paper. Christie, *et al.*[6] reported a constant high collection efficiency for NO_2 by adding 0.1% sodium arsenite to aqueous sodium hydroxide absorbing solutions. Presumably the $NaAsO_2$ acts as an electron donor to increase the rate of conversion of NO_2 to NO_3^-. Thus, the arsenite modification of the original reference method appeared to have overcome its major deficiency. It was therefore chosen as one of the candidate methods.

Experimental Procedure

Test Atmosphere Generation

Test atmospheres containing known amounts of NO_2 in addition to NO_2 in combination with known amounts of NO and CO_2 were generated by flow dilution of standards with purified air using the apparatus shown in Figure 1.

Nitrogen Dioxide. Two gravimetrically calibrated NO_2 permeation devices, prototypes of the National Bureau of Standards (NBS) standard reference material No. 1629, were used. The devices had permeation rates of 1.082 ± 0.001 and 0.808 ± 0.001 μg NO_2/min at 25.0 ± 0.1°C.

Nitric Oxide. An analyzed cylinder of NO in N_2 was used. The contents were first analyzed for NO by gas phase titration (GPT) with O_2[10] and found to contain 92.4 ± 1.1 ppm NO. The NO concentration was verified by comparing, on a chemilu-

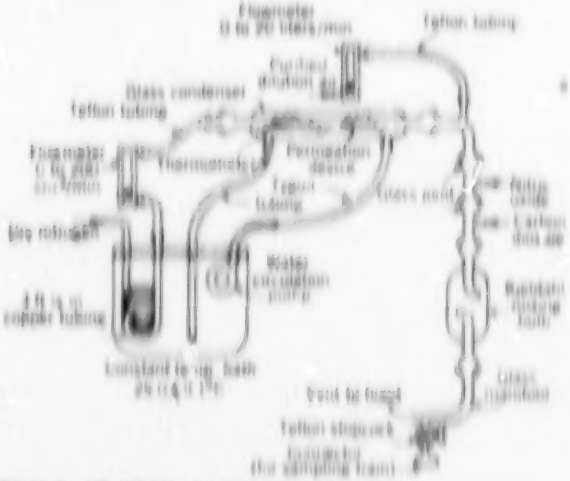

Figure 1. NO_2, NO, CO_2, and purified air generation system.

ent NO/NO_2, NO_x monitor, the NO_2 produced during GPT with the output of an NO_2 permeation device. The NO_2 concentration from these two sources agreed within 2% of the mean. The cylinder was also analyzed for NO_2 using the triethanolamine quatured sulfite method,[5] and found to contain 1.8 ± 0.1 ppm NO_2. The portion of the NO_2 coming from the NO cylinder was 0.5 to 7.0% of the NO_2 in the test atmosphere and was accounted for in calculating the NO_2 concentration.

Carbon Dioxide — NBS standard reference material No. 1674 was used. This material is CO_2 in N_2 compressed in cylinders. The CO_2 concentration was 70,300 ± 100 ppm CO_2.

Purified Dilution Air — This air was obtained by passing compressed (house) air through silica gel for drying, treating with O_3 to convert any NO to NO_2, and by passing through activated charcoal (6–14 mesh) and molecular sieve (6–16 mesh, type 4A) to remove NO_x, hydrocarbons, O_3, acid traces of water. Carbon dioxide was removed by passing the air through a trap containing approximately 1 kg of Ascarite.

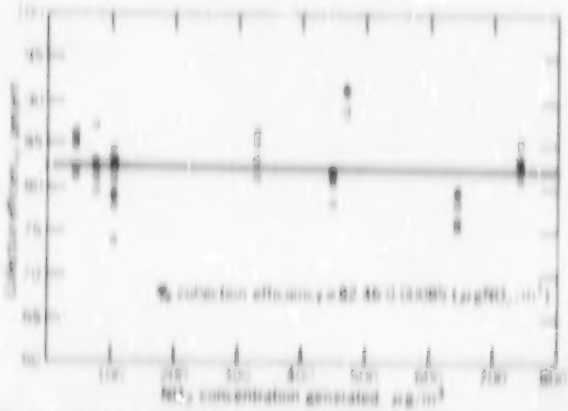

Figure 2. Percent collection efficiency of the arsenite method as a function of NO_2 concentration.

Sodium Arsenite Method

Details of sampling, analysis and calibration procedures are specified in an EPA Report.[3]

Samples were collected in quintuplicate by attaching 5 polypropylene absorption tubes containing 50 ml of 0.1*N* NaOH and 0.1% $NaAsO_2$ to a common manifold. Each absorption tube was equipped with a glass tube restricted orifice (diameter 0.3 to 0.8 mm) to disperse the gas. Sample flow rate was controlled at approximately 200 cm^3/min by using a 27-gauge hypodermic needle as a critical orifice. Sampling time was about 30 hr. Flows were measured with a soap bubble flowmeter.

Samples were analyzed for NO_2 by a diazotization coupling reaction. The absorbance of the pink dye produced was measured at 540 nm and concentration (in μg NO_2/ml) read from a calibration curve. Sodium nitrite was used as the source of NO_2 for calibration.

Results and Discussion

Since the method analyses up to the establishment of the relationship between NO_2 in the air sample and NO_2 in solution, i.e., the NO_2 collection efficiency is necessary, investigating the collection efficiency was essential prior to an in-depth evaluation because the original reference method had exhibited a 50% non-linear variation in collection efficiency over the range 30 to 750 μg/m^3.[1]

Sampling System

The collection efficiency was determined by sampling 8 different test atmospheres ranging from 44 to 743 μg NO_2/m^3. Collected samples were analyzed as described in the Experimental Procedure. The collection efficiency, in percent, was calculated as

$$\text{collection efficiency, \%} = \frac{\text{NO}_2 \text{ analyzed}}{\text{NO}_2 \text{ generated}} \times 100$$

The data are shown in Figure 2 as a function of NO_2 concentration generated. The least squares regression equation for the data is given in Figure 2. The intercept, 82.46, represents the collection efficiency, and the slope of the straight line is 0.00880. The relative standard deviation of the data points is 4.7%. Thus, the collection efficiency can be considered as constant and the data show that the variable collection efficiency of the original reference method has indeed been corrected by the arsenite modification.

Analytical System

The diazotization coupling reaction used to detect nitrite in this analysis is well documented in the literature. However, certain parameters in the analysis were deemed worthy of investigation to insure that the arsenite modification had not affected them.

The optimum pH and time for color development were investigated and found to be 2.0 and 10 min, respectively; the wavelength of maximum absorbance was found to be 540 nm; color was stable for at least 30 min after development.

The stability of a collected NO_2 sample was investigated by analyzing a sample containing approximately 0.50 μg NO_2/ml (equivalent to 1081 μg NO_2/m^3) at 0, 1, 4, and 11 days after collection. No significant change in concentration was found.

Ruggedness Testing

The next phase of the evaluation involved a test designed to determine the sensitivity of important operational parameters to slight changes similar to those encountered in normal use. This type of evaluation is called ruggedness testing. It is accomplished by conducting a series of experiments in which selected parameters are varied at two levels: the nominal level stated in the method write-up and a challenging level. The results obtained using the nominal procedure are compared with the results obtained using the variation in order to determine the effect of the variable.

An ingenious scheme for determining the individual effects of variations in several parameters with a minimum number of experiments has been described by Youden.[10]

It should be noted that the results of the ruggedness test will not completely describe the effect of varying a given parameter. The variables chosen for study are listed in Table I. The nominal value is listed first followed by the challenging value. The CO concentration was studied because it had been reported[1] that CO was a negative interferent in the arsenite method at the 9880 ppm level. Since we were concerned with lower ambient levels, the nominal CO concentration was chosen as that which existed during the experiments. (The purified air did not contain an ascarite scrubber for these experiments.) The challenging value was then produced by adding 100 ppm CO to this atmosphere.

It should be noted that the system blank is unlike the customary blank in which the concentration of NO_2 is zero. The

Table I. Ruggedness test results.

Rank	Factor	Difference, %
1.	CO_2 concentration Ambient vs. ambient + 500 ppm	18.1
2.	Flow rate 280 cm³/min vs. 300 cm³/min	14.1
3.	Orifice size 0.6 mm vs. 1.0 mm	(+) 2.6
4.	NO concentration 85 μg/m³ vs. 700 μg/m³	(+) 1.9
5.	$NaAsO_2$ concentration 1.0 g/l vs. 0.5 g/l	(+) 1.5
6.	Temperature 25°C vs. 35°C	1.2
7.	Experimental blank	1.1

system blank is merely a mathematical difference of all the variable conditions in the experiment.

The results of the ruggedness test, shown in Table I, are expressed in percent. Calculations were made by dividing the concentration found (corrected for a collection efficiency of 82%) by the concentration of NO$_2$ generated. This normalization of results was necessary before the effect of the different parameters could be determined because the method is obviously sensitive to NO$_2$.

The results show that the system blank is only 1.1%. This means that the method, without any variation, accurately measures NO$_2$ over the range 85–700 μg/m³. The values obtained for orifice size, NO$_2$ and $NaAsO_2$ concentration, and absorber temperature are −2.6 to +1.2% and are similar to the blank indicating that variations in these parameters do not significantly affect the method response.

Table II. NO_2, NO, and CO_2 concentrations selected for study.

	Minimum	Mid-range	Maximum
NO	50 μg/m³ (0.03 ppm)	180 μg/m³ (0.15 ppm)	310 μg/m³ (0.25 ppm)
NO_2	50 μg/m³ (0.03 ppm)	150 μg/m³ (0.08 ppm)	250 μg/m³ (0.13 ppm)
CO_2	300 ppm	450 ppm	600 ppm

The most significant effect is due to CO_2 concentration. The positive value of 18.1% indicates that the recovery of NO$_2$ is significantly reduced by the presence of an additional 300 ppm CO_2 (over ambient) in the air sample. Thus, CO_2 is a negative interferent in the method. Increasing the sample flow rate from 280 to 300 cm³/min reduces the NO$_2$ recovery by 14%. Subsequent experiments on quantitation of the effect of flow rate show that the recovery is constant from 200 to 270 cm³/min and then it starts to decrease.[12] Since 270 cm³/min is significantly above the flow rate specified in the method, 180–230 cm³/min, no tightening of this specification is required.

Interferences

Because the ruggedness test results show that CO_2 is an interferent in the method and because NO had previously been identified as a positive interferent,[7] a series of experiments was conducted to quantify the effect of NO and CO_2 concentration on the recovery of NO$_2$. Test atmospheres containing combinations of NO, CO_2, and NO$_2$, at a constant concentration of each substance, were sampled according to the method. Three levels were chosen to demonstrate the effect of each material and to show if the effects were linear or curvilinear over the range of interest. This plan results in 27 experiments (3 pollutants × 9 concentrations). Each NO, CO_2, and NO$_2$ concentration was held constant during an experiment, rather than varied with time as would occur in ambient air, because accurate concentration control is difficult under the latter conditions. It is felt that the constant-concentration conditions represent a reasonable approximation to ambient conditions and, therefore, provide a useful means for evaluating interferences to the method.

Nitric oxide and nitrogen dioxide levels for the experiments were determined from examination of EPA ambient data collected by chemiluminescence and continuous colorimetric procedures.[13] Carbon dioxide levels were determined from the literature.[11]

Maximum, mid-range, and minimum concentrations were chosen for each of the three parameters, the nominal values of which are given in Table II. The mid-range values were chosen to approximate average ambient NO and CO_2 concentrations and the ambient air standard for NO$_2$ (0.05 ppm or 100 μg/m³).

The experiments were conducted in random order. An analysis of variance on the data shows a linear relationship between method response and generated levels of CO_2 and NO. As the levels of CO_2 and NO increase the slopes decrease and increase, respectively, and the slopes were significantly different at all three levels. The average method response values are given in Table III. Several examples on the use of this table are in order. At 180 μg NO$_2$/m³ the middle row of figures in the first block gives the method response at 0.03 ppm CO_2 for each of the three NO concentrations. The figure at the bottom of each NO column is the average response over all three NO$_2$ levels for one CO_2 concentration. The mean value is the average over all NO$_2$ and NO levels for 600 ppm CO_2. The same pattern follows for the other two blocks.

Table III. Average values of method response.

NO (μg/m³)	CO_2 (ppm) 300			450			600			
NO_2 (μg/m³)	50	180	310	50	180	310	50	180	310	
50	52.3	62.0	57.3	50.2	52.8	58.1	47.8	50.1	53.0	53.0
150	154.7	165.7	174.7	151.6	177.5	192.5	140.3	139.8	141.9	156.0
250	256.3	275.2	280.3	247.3	254.7	257.0	228.0	237.9	264.2	255.5
NO + CO_2	154.6	167.6	169.5	149.7	161.3	158.1	138.1	142.4	155.0	Grand Mean
Mean		163.9			156.7			145.4		155.3

bon (0% and 500 ppm CO_2). As the nominal CO_2 level is increased from 200 to 350 ppm (75% increase), the mean method response decreases by 9%, as seen in the lower margin. A further increase in the CO_2 level from 350 to 500 ppm results in a further drop of 7% in the mean method response. For each level of NO, the decrease in average method response due to increasing CO_2 differs from that seen in the NO × CO_2 margin. As the nominal NO level is increased from 50 to 180 μg/m³ (over 300%), the average method response (over all NO_2 and CO_2 levels) increases by 6%. A further increase in the NO level from 180 μg/m³ to 310 μg/m³ (67% increase) results in a 3% increase in the average method response.

Table IV. Average bias (μg/m³) over all NO, concentrations.

NO (μg/m³)	CO_2 (ppm) 200	350	500	
50	9.1	4.3	−2.0	3.8
180	21.9	15.8	3.4	13.7
310	23.3	14.4	9.7	16.1
	18.1	11.5	3.7	11.2

Table IV shows that the overall bias of the arsenite method, calculated by taking the difference (method response − generated NO) and averaging over all values, is 11.2 μg/m³. The 95% confidence interval for this bias is 7.5–12.2 μg/m³ indicating that this bias is real and significantly different from zero. A more detailed analysis of these data can be found in an earlier publication.[7]

Thus, the combination of ambient NO, and CO_2 levels will produce a positive bias into the arsenite method. However, the magnitude of this bias (10% of the ambient air standard) is not large enough to warrant modification of the method to remove the interference.

Conclusions

The arsenite method has a constant high collection efficiency over the entire range of the method. The method is insensitive to normal variations in orifice bubbler diameter, temperature of the absorbing solution during sampling, concentration of sodium arsenite, and sample flow rate. Nitric oxide and carbon dioxide are positive and negative interferents, respectively. However, at ambient concentrations the average effect of these interferents is minor.

The method has been subjected to a collaborative test and found to be a reliable procedure for measurement of NO_2 in ambient air.[11]

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References

1. *Federal Register* 36, 8186, April 30, 1971.
2. J. H. Hauser, *J. Air Poll. Control Assoc.* 8, 100 (1972).
3. G. F. Merryman, *et al.*, *Environ. Sci. Technol.* 7, 1009 (1973).
4. J. H. Hauser, R. S. Brief, "Evaluation of the Jacobs-Hochheiser method for determining ambient nitrogen dioxide," *Atmosphere* (1), 43 (1973).
5. *Federal Register* 38, 15174, June 8, 1973.
6. Forest R. G. Margeson, J. H., "An Evaluation of the TGS ANSA Procedure for Determination of Nitrogen Dioxide in Ambient Air," EPA Report No. 650/4-74-047, Nov. 1974.
7. R. C. Ellis, J. H. Margeson, "Evaluation of Triethanolamine Procedure for Determination of Nitrogen Dioxide in Ambient Air," EPA Report No. 650/4-74-031, July 1974.
8. A. A. Christie, *et al.*, "Field methods for the determination of nitrogen dioxide in air," *Analyst* 98, 833 (1973).
9. M. E. Beard, J. H. Margeson, "An Evaluation of Arsenite Procedure for Determination of Nitrogen Dioxide in Ambient Air," EPA Report No. 650/4-74-048, Nov. 1974.
10. W. J. Youden, *Statistical Techniques for Collaborative Tests*, Association of Official Analytical Chemists, Washington, D. C. 1967, pp. 20–32.
11. J. E. Clarke, *Atmos. Environ.* 8, 375 (1974).
12. M. E. Beard, *et al.*, "Evaluation of Effects of NO_2, CO_2, and Sampling Flow Rate on Arsenite Procedure," EPA Report No. 650/4-75-019, April 1975.
13. F. F. Constant, Jr., *et al.*, "Collaborative Testing of Methods for Measurements of NO_2 in Ambient Air (Sodium Arsenite Procedure)," EPA Report No. 650/4-74-039a, June 1974.

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